## A Cu<sup>II</sup>-nitrite That Exhibits Change of Nitrite Binding Mode and Formation of Cu<sup>II</sup>-nitrosyl Prior to NO Evolution

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Figure S1. FTIR spectrum of HL2 in KBr disk in the range 4000 cm<sup>-1</sup>-400 cm<sup>-1</sup>.



Figure S2. ESI mass spectra of HL2 taken in CH<sub>3</sub>CN, peak at m/z = 197.07 corresponding to  $\{HL2+H^+\}$ .



Figure S3. <sup>1</sup>H NMR spectrum of HL2 in CDCl<sub>3</sub>.



Figure S4. FTIR spectrum of [(L2)CuONO], 2 in KBr disk in the range 4000 cm<sup>-1</sup>-400 cm<sup>-1</sup>



Figure S5. FTIR spectrum of [(L2)Cu(OAc)], 3 in KBr disk in the range 2000 cm<sup>-1</sup>-400 cm<sup>-1</sup>.



Figure S6. FTIR spectrum of 4 (top) and [Bu<sub>4</sub>N][(L2)Cu(CH<sub>3</sub>CN)(NO<sub>2</sub>)] (bottom) in KBr disk.



**Figure S7.** <sup>1</sup>H NMR spectrum of  $[Co(Cp)_2][(L2)Cu^I(NO_2)(CH_3CN)]$  in CD<sub>3</sub>CN.



Figure S8. Electronic absorption spectra of 1(Black), 2 (red), 3 (green) in CH<sub>3</sub>OH solvent.



Figure S9. Electronic absorption spectra of (A) 1(Black), 2 (red), 3 (green) in CH<sub>3</sub>CN solvent and of (B) L2 liagnd, NaL2, a mixture of NaL2 and  $[Zn(H_2O)_6](ClO_4)_2$  and a mixture of NaL2 +  $[Zn(H_2O)_6](ClO_4)_2$  +  $[Bu_4N]NO_2$  confirming assignment of n-p\* and p-p\* transitions as mentioned in the manuscript

compound	$\lambda_{\rm max}$ , nm ( $\epsilon$ M <sup>-1</sup> cm <sup>-1</sup> )	Ref.
<b>1</b> : CH <sub>3</sub> OH	262(12140), 270sh(11260), 300(9245), 315sh	This work
	(8660), 648(195)	
CH <sub>3</sub> CN	245(15650), 265sh(13040), 311(10140), 620(165)	
<b>2</b> : CH <sub>3</sub> OH	262(10232), 270sh(9840), 293(7685), 355sh	This work
	(2735), 613(95).	
CH <sub>3</sub> CN	245(16035), 265sh(12899), 303(10400), 365sh	
	(2477), 593 (125).	
<b>3</b> : CH <sub>3</sub> OH	262(11060), 270sh(10400), 298(9175), 627(155)	This work
-		
CH <sub>3</sub> CN	245 (16980), 265 sh(14870), 302(11910),	
	610(120)	
[(L1)CuCl] <sub>n</sub> : CH <sub>3</sub> OH	258 (10400), 299 (5500), 310 (5590), 326 sh	Ref. 13
	(5426), 455 sh (81), 642 (103)	
[(L1)Cu(ONO)] : CH <sub>3</sub> OH	257 (14480), 298 (8540), 310 (8280), 327 sh	Ref. 13
	(7730), 613 (157)	
[(L1)Cu(CH <sub>3</sub> CO <sub>2</sub> )]: CH <sub>3</sub> OH	259 (15420), 296 sh (8920), 310 sh (8500), 330	Ref. 13
	(7600), 627(143)	

**Table S1.** Electronic absorption spectral data of the complexes 1-3 and the corresponding complexes of  $L1^{-}$  analogue measured at 298 K.



**Figure S10.** Electronic absorption spectral changes during transformation of[(L2)CuCl(H<sub>2</sub>O)], **1** (black trace)  $\rightarrow$  **2** (red trace) when titrating a CH<sub>3</sub>CN solution of **1** with a CH<sub>3</sub>CN solution of (n-Bu<sub>4</sub>N)NO<sub>2</sub>.



**Figure S11.** Cyclic voltammogram of  $[(L2)Cu(H_2O)Cl]$ , **1** (orange) in CH<sub>3</sub>CN containing (Bu<sub>4</sub>N)ClO<sub>4</sub> as supporting electrolyte at 298 K at a Pt working electrode at a scan rate of 50 mV/s using SCE reference electrode.



**Figure S12.** (i) DFT-optimized structure (ii) HOMO (iii) LUMO of [(L2)Cu(ONO)], **2**. Atomic contribution of HOMO, Cu 7%,  $N_{NO2}^-$  1%,  $O_{NO2}^-$  3%,  $N_{amide}$  48%  $O_{amide}$  25%. Atomic contribution of LUMO Cu 51%,  $N_{NO2}^-$  1%,  $O_{NO2}^-$  7%,  $N_{amide}$  9%  $O_{amide}$  1%. NBO calculations shows that the copper atom in the complex has a d<sup>9</sup> configuration, indicating its oxidation state is +2 [core] 4S( 0.38)3d( 9.44)4p( 0.40). Energy of HOMO = -6.31 eV, LUMO = -3.31 eV.



**Figure S13.** (i) DFT-optimized structure (ii) HOMO (iii) LUMO of  $[(L2)Cu^{I}(\kappa^{2}-ONO)]^{-}$ , (I). Atomic contribution of HOMO, Cu 68%, N<sub>NO2</sub><sup>-</sup> 1%, O<sub>NO2</sub><sup>-</sup> 5%, N<sub>amide</sub> 7% O<sub>amide</sub> 2%. Atomic contribution of LUMO Cu 2%, N<sub>NO2</sub><sup>-</sup> 0%, O<sub>NO2</sub><sup>-</sup> 0%, N<sub>amide</sub> 3%, O<sub>amide</sub> 5%. NBO calculations shows that the copper atom in the complex has a d<sup>10</sup> configuration, indicating its oxidation state as +1 [core] 4S( 0.45)3d( 9.81)4p( 0.27). Energy of HOMO = -4.73 eV, LUMO= -1.07 eV.



**Figure S14.** (i) DFT-optimized structure (ii) HOMO (iii) LUMO of  $[(L2)Cu^{I}(\kappa^{1}-NO_{2})]^{-}$ , (II). Atomic contribution of HOMO Cu 57%,  $N_{NO2}^{-}6\%$ ,  $O_{NO2}^{-}11\%$ ,  $N_{amide}5\%$   $O_{amide}1\%$ . Atomic contribution of LUMO Cu 2%,  $N_{NO2}^{-}1\%$ ,  $O_{NO2}^{-}2\%$ ,  $N_{amide}3\%$   $O_{amide}5\%$ . NBO calculations shows that the copper atom in the complex has a d<sup>10</sup> configuration, indicating its oxidation state is +1, [core] 4S( 0.43)3d( 9.83)4p( 0.29). Energy of HOMO = -4.92 eV, LUMO = -1.12 eV.



**Figure S15.** (i) DFT-optimized structure (ii) HOMO (iii) LUMO of  $[(L2)Cu^{1}(\kappa^{1}-NO_{2})(CH_{3}CN)]^{-}$ , (III). Atomic contribution of HOMO Cu 51%,  $N_{NO2}^{-}$  10%,  $O_{NO2}^{-}$  11%,  $N_{amide}$  11%  $O_{amide}$  6%. Atomic contribution of LUMO Cu 1%,  $N_{NO2}^{-}$  0%,  $O_{NO2}^{-}$  0%,  $N_{amide}$  3%  $O_{amide}$  4%. NBO calculations shows that the copper atom in the complex has a d<sup>10</sup> configuration, indicating its oxidation state is +1 [core] 4S( 0.30)3d( 9.80)4p( 0.44). Energy of HOMO = -4.55 eV, LUMO = -0.97 eV.

## Experimental setup for standardization of [NO(g)] in CH<sub>3</sub>CN

Potentials are measured using same cell setup as kept for measurement of NO generation from the reduced sample of **2** in 15 mL CH<sub>3</sub>CN. Pure NO(g) has been taken using a gas tight syringe. After adding NO(g) to the cell, the CV scans were started to collect until it reaches to a maximum then decreases (as shown below for the 54 ppm NO solution). The CV scan having maximum  $i_{pc}$  has been considered to get the calibration curve. It can be assumed that the NO(g) injected to the CH<sub>3</sub>CN solvent is get absorbed and owing to this reason a linear calibration curve (Fig. S14) has been obtained. For our experiment with reduced **2** at the most 1 mL NO(g) will get liberated.



Cyclic voltammograms of 0.6 ml NO (54 ppm) dissolved in 15 mL CH<sub>3</sub>CN solution containing  $(Bu_4N)CIO_4$  as supporting electrolyte at 298 K at a platinum working electrode at a scan rate of 300 mV/s using SCE as reference electrode.



Figure S16. Standardization plot of NO(g)



**Figure S17.** Electronic absorption spectra of [Co(TPP)] (blue trace) and [Co(TPP)NO] (pink trace)



**Figure S18.** FTIR spectra of [Co(TPP)] (blue trace) and [Co(TPP)NO] (orange trace)



**Figure S19.** Spin quantification considering complex **2** as a standard (red and green traces are considered from Figure 7A). The [Area under the green trace]/[area under the red trace] multiplied by 100 = 5.5% i.e. the Cu(II) formed during electrolysis of CH<sub>3</sub>CN solution of **2** via disproportionation.



**Figure S20.** X-Band EPR spectra measured at 77 K in CH<sub>3</sub>CN solution: of reduced **2** (green), reduced **2** plus CH<sub>3</sub>CO<sub>2</sub>H (black trace) and then same solution keeping at 77 K after 5 minute intervals (pink, red and cyan trace) showing slight increase of signal intensity. Green trace of reduced species displays *isotropic* spectrum profile, whereas other traces obtained after CH<sub>3</sub>CO<sub>2</sub>H addition are *axial* in nature like the authentic **3** displays. Spectrometer settings: microwave frequency = 9.416 GHz, power = 10 mW, modulation frequency = 100 kHz; modulation amplitude = 5 G.



DFT optimized structure of IV<sup>SS</sup>



**Figure S21.** HOMO, HOMO-1, HOMO-2 and LUMO of singlet  $[(L2)Cu^{II}(NO)]^+$ ,  $IV^{SS}$ : Atomic contribution of HOMO Cu 5%, N<sub>NO</sub> 7%, O<sub>NO</sub> 6%, N<sub>amide</sub> 44% O<sub>amide</sub> 23%, atomic contribution of HOMO-1 Cu 5%, N<sub>NO</sub> 9%, O<sub>NO</sub> 8%, N<sub>amide</sub> 24% O<sub>amide</sub> 39%, atomic contribution of HOMO-2 Cu 11%, N<sub>NO</sub> 7%, O<sub>NO</sub> 7%, N<sub>amide</sub> 9% O<sub>amide</sub> 38%, atomic contribution of LUMO Cu 19%, N<sub>NO</sub> 36%, O<sub>NO</sub> 20%, N<sub>amide</sub> 5% O<sub>amide</sub> 1%.



**Figure S22.** (a) DFT-optimized structure, (b) HOMO and (c) LUMO of of triplet  $[(L2)Cu^{II}(NO)]^+$ ,  $IV^{TS}$ : Atomic contribution of HOMO Cu 10%, N<sub>NO</sub> 31%, O<sub>NO</sub> 19%, N<sub>amide</sub> 8% O<sub>amide</sub> 9%. Atomic contribution of LUMO Cu 2%, N<sub>NO</sub> 59%, O<sub>NO</sub> 36%, N<sub>amide</sub> 0% O<sub>amide</sub> 0%.



**Figure S23.** Energy profile of  $IV^{SS}$ ,  $IV^{TS}$ ,  $V^{SS}$  and  $V^{TS}$ 



Figure S24. HOMO, HOMO-1, HOMO-2 and LUMO of singlet  $[(L2)Cu^{II}(NO)(CH_3CN)]^+$ ,  $V^{SS}$ : Atomic contribution of HOMO Cu 6%, N<sub>NO</sub> 6%, O<sub>NO</sub> 4%, N<sub>amide</sub> 43% O<sub>amide</sub> 24%, atomic contribution of HOMO-1 Cu 4%, N<sub>NO</sub> 9%, O<sub>NO</sub> 8%, N<sub>amide</sub> 24% O<sub>amide</sub> 39%, atomic contribution of HOMO-2 Cu 11%, N<sub>NO</sub> 7%, O<sub>NO</sub> 7%, N<sub>amide</sub> 9% O<sub>amide</sub> 36%, atomic contribution of LUMO Cu 21%, N<sub>NO</sub> 34%, O<sub>NO</sub> 19%, N<sub>amide</sub> 5% O<sub>amide</sub> 2%.



**Figure S25.** (i) DFT-optimized structure, (ii) HOMO and (iii) LUMO of triplet  $[(L2)Cu^{II}(NO)(CH_3CN)]^+$ ,  $V^{TS}$ : Atomic contribution of HOMO Cu 2%, N<sub>NO</sub> 36%, O<sub>NO</sub> 59%, N<sub>amide</sub> 1% O<sub>amide</sub> 1%. Atomic contribution of LUMO Cu 1%, N<sub>NO</sub> 36%, O<sub>NO</sub> 62%, N<sub>amide</sub> 0%.



Figure S26. Calculated IR spectrum of [(L2)Cu<sup>II</sup>(NO)] model considering singlet state, IV<sup>SS</sup>



Figure S27. Calculated IR spectrum of [(L2)Cu<sup>II</sup>(NO)] model considering triplet state, IV<sup>TS</sup>



**Figure S28.** Calculated IR spectrum of [(L2)Cu<sup>II</sup>(CH<sub>3</sub>CN)(NO)] model considering singlet state, V<sup>SS</sup>



**Figure S29.** Calculated IR spectrum of  $[(L2)Cu^{II}(CH_3CN)(NO)]$  model considering triplet state,  $V^{TS}$ 



**Figure S30.** DFT-optimized structure of V<sup>SS</sup> (top) and V<sup>TS</sup> (bottom) and their HOMOs considering 6-311G(d,p) basis set for all atoms. Color code: C black, N blue, O red, S yellow, H pearl, Cu light orange. Atomic composition for HOMO (LUMO) in % of V<sup>SS</sup>: 5(3) Cu, 5(58) N<sub>NO</sub>, 4(35) O<sub>NO</sub>, 42(0) N<sub>amide</sub>, 30(0) O<sub>amide</sub> and of V<sup>TS</sup> is 1(0) Cu, 56(63) N<sub>NO</sub>, 34(36) O<sub>NO</sub>, 5(0) N<sub>amide</sub>, 3(0) O<sub>amide</sub>.



**Figure S31.** Calculated IR spectrum of  $[(L2)Cu^{II}(CH_3CN)(NO)]$  model considering singlet state ( $V^{SS}$ ) and 6-311G(d,p) basis set for all atoms.



**Figure S32.** Calculated IR spectrum of  $[(L2)Cu^{II}(CH_3CN)(NO)]$  model considering triplet state ( $V^{TS}$ ) and 6-311G(d,p) basis set for all atoms.